

Compound Semiconductor Electrodeposition via Ligand Stabilized Cations over Large pH Ranges

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Electrodeposition is an efficient and inexpensive route to thin or thick films of materials appropriate to this technique. While generally metallic elements and alloys are deposited electrochemically, both compound semiconductors such as Bi_2Te_3 and precursors to compound semiconductors, such as Co/Sb mixtures have been prepared using electrodeposition.

In many electrodeposition processes, both for metals and compounds, good deposits can be obtained only if the pH of the plating solution remains within a narrow range; and often electrodeposition conditions include strongly acid or basic solutions. Furthermore, many cations are stable only within limited pH ranges, putting deleterious constraints on the deposition process. For example, deposition of Bi_2Te_3 is typically carried out in strong acid solution, in which the solubility of Te is only moderately high for the Te^{+6} oxidation state. Starting from a moderately concentrated Te^{+6} solution, electrochemical reduction will produce nearly insoluble tellurous acid as a precipitate as well as an electrodeposit which may be bismuth and/or bismuth telluride. This problem can be alleviated by going to very dilute solutions in which the tellurium concentration does not exceed the solubility of Te^{+4} .

It is well known that the solubility of Bi^{+3} and Sb^{+3} is significantly enhanced by formation of their complexes with alpha hydroxy carboxylic acids, such as tartaric or citric acid. Furthermore, while simple carboxylic acid salts of Bi^{+3} and Sb^{+3} such as the acetate are rather insoluble in water, addition of excess acetic acid or an acetate salt significantly increases the solubility of Bi^{+3} and Sb^{+3} acetates. Other ligands are also known to be effective at increasing the solubility of cations as well as stabilizing their solubility over larger pH ranges. The goal of the present study was to develop a technique for fairly rapid and efficient electrodeposition of Bi_2Te_3 and its derivatives such as $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$.

This paper reports the application of ligand stabilization to achieve much higher solubilities of Bi^{+3} , Sb^{+3} and Te^{+4} , and other cations over a broad pH range. This in turn allows pH to be adjusted as a deposition parameter to affect the reduction potential necessary for the various complexes, and to assist in control of the film stoichiometry by modification of the deposition parameters. This paper will also report the influence of deposition parameters on crystallographic order in compound semiconductors and deposition of mixtures with controlled homogeneity.